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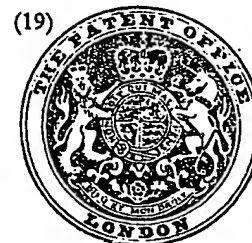
PATENT SPECIFICATION

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DRAWINGS ATTACHED

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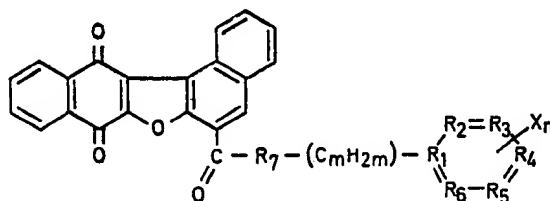
(54) BENZOBRAZANQUINONE PIGMENTS

(71) We, XEROX CORPORATION of Rochester, New York 14603, United States of America, a Body Corporate organised under the laws of the State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates, in general, to benzobrazanquinone pigments, and, more especially, to the use of said pigments in photoelectrophoretic imaging systems.

There has been recently developed an electrophoretic imaging system capable of producing color images which utilizes single-component photoconductive particles. This process is described in detail and claimed in U.S. Patents 3,384,565, 3,384,566 and 3,384,488. In such an imaging system, variously colored light absorbing particles are suspended in a non-conductive liquid carrier. The suspension is placed between electrodes, subjected to a potential difference and exposed to an image. As these steps are completed, selective particle migration takes place in image configuration, providing a visible image at one or both of the electrodes. An essential component of the system is the suspended particles which must be electrically photosensitive and which apparently undergo a net change in charge polarity upon exposure to activating electromagnetic radiation, through interaction with one of the electrodes. In a monochromatic system, particles of a single color are used, producing a single colored image equivalent to conventional black-and-white photography. In a polychromatic system, the images are produced in natural color because mixtures of particles of two or more different colors which are each sensitive to light of a specific wavelength or narrow range of wavelengths are used. Particles used in this system must have both intense pure colors and be highly photosensitive. The pigments of the prior art often lack the purity and brilliance of color, the high degree of photosensitivity, and/or the preferred correlation between the peak spectral response and peak photosensitivity necessary for use in such a system.

According to the present invention there is provided a compound having the general formula:



wherein:

R₇ is NH, O, S or Se;

Each of the R's R₁ to R₆ independently is N or CH, from 0—4 of the R's being R₁ to R₆ being N;

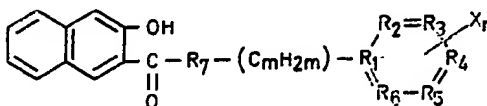
Each X independently is alkyl (for example CH₃ or C₂H₅), aryl, alkoxy (for example OCH₃ or OC₂H₅), carboxylic acid, carboxylic ester (for example CO₂CH₃ or CO₂C₂H₅), CF₃, NO₂, CN, SO₂NH₂, SO₂NHC₆H₅, Cl, Br, F, I or H;

m is a positive integer from 0—10 when $R_7 \neq \text{NH}$ and from 1—10 when $R_7 = \text{NH}$; and

n is a positive integer from 1—5. This particular class of benzobrazanquinone pigments has been found to have electrically photosensitive or photomigratory characteristics such as to make them especially useful in photoelectrophoretic imaging systems.

While any of the class of benzobrazanquinone pigments having the above-described general formula may be used in photoelectrophoretic imaging systems, it is preferred to employ those compounds wherein $X = \text{H}$ or CH_3 ; wherein $m = 1$ or 2 ; and wherein from 1 to 3 of the R 's R_1 to $R_6 = \text{N}$, since the materials have especially pure color and are highly photosensitive for use in electrophoretic imaging processes. Optimum results are achieved when $X = \text{H}$. The benzobrazanquinone pigments of the present invention may have other materials added thereto to sensitize, enhance, synergize, or otherwise modify their properties.

The compounds of the formula given above may be made by reaction 2,3-dichloro-1,4-naphthoquinone with an anilide or ester, having the formula:



wherein, R_1 to R_7 , X , m and n are as defined above.

The compounds produced by the above reaction have the common characteristics of a brilliant, intense yellow or orange color, of insolubility in water and the common organic solvents, e.g., benzene, toluene, acetone, carbon tetrachloride, chloroform, alcohols, and aliphatic hydrocarbons; and of unusually high photosensitive response.

The use of the benzobrazanquinone pigments of the present invention in photoelectrophoretic imaging processes may be further understood by reference to the single figure of the accompanying drawing which shows an electrophoretic imaging system.

Referring now to the figure, there is seen a transparent electrode generally designated 1 which, in this instance, is made up of a layer of optically transparent glass 2 overcoated with a thin optically transparent layer 3 of tin oxide, commercially available under the name NESA (registered Trade Mark) glass. This electrode will hereafter be referred to as the "injecting" electrode. Coated on the surface of injecting electrode 1 is a thin layer 4 of finely divided photosensitive particles dispersed in an insulating liquid carrier. The term "photosensitive", for the purposes of this application, refers to the properties of a particle which, once attracted to the injecting electrode, will migrate away from it under the influence of an applied electric field when it is exposed to actinic electromagnetic radiation. For a detailed theoretical explanation of the apparent mechanism of operation of the invention, the reader is referred to the above-mentioned U.S. Patents 3,384,565, 3,384,566 and 3,384,488. Liquid suspension 4 may also contain a sensitizer and/or a binder for the pigment particles which is at least partially soluble in the suspending or carrier liquid as will be explained in greater detail below. Adjacent to the liquid suspension 4 is a second electrode 5, hereinafter called the "blocking electrode", which is connected to one side of the potential source 6 through a switch 7. The opposite side of potential source 6 is connected to the injecting electrode 1 so that when switch 7 is closed, an electric field is applied across the liquid suspension 4 between electrodes 1 and 5. An image projector made up of a light source 8, a transparency 9 and a lens 10 is provided to expose the dispersion 4 to a light image of the original transparency 9 to be reproduced. Electrode 5 is made in the form of a roller having a conductive central core 11 connected to the potential source 6. The core is covered with a layer of a blocking electrode material 12, which may be Baryta paper. The pigment suspension is exposed to the image to be reproduced while a potential is applied across the blocking and injecting electrodes by closing switch 7. Roller 5 is caused to roll across the top surface of injecting electrode 1 with switch 7 closed during the period of image exposure. This light exposure causes exposed pigment particles originally attracted to electrode 1 to migrate through the liquid and adhere to the surface of the blocking electrode, leaving behind a pigment image on the injecting electrode surface which is a duplicate of the original transparency 9. After exposure, the relatively volatile carrier liquid evaporates off, leaving behind the pigment image. This pigment image may then be fixed in place as, for example, by placing a lamination over its top surface or by virtue of a dissolved binder material in the carrier liquid such as paraffin wax or other suitable binder that comes out of

solution as the carrier liquid evaporates. About 3% to 6% by weight of paraffin binder in the carrier has been found to produce good results. The carrier liquid itself may be liquified paraffin wax or other suitable binder. In the alternative, the pigment image remaining on the injecting electrode may be transferred to another surface and fixed thereon. As explained in greater detail below, this system can produce either monochromatic or polychromatic images depending upon the type and number of pigments suspended in the carrier liquid and the color of light to which this suspension is exposed in the process.

Any suitable insulating liquid may be used as the carrier for the pigment particles in the system. Typical carrier liquids are decane, dodecane, n-tetradecane, paraffin, beeswax or other thermoplastic materials, Sohio Odorless Solvent 3440, (a kerosene fraction available from Standard Oil Company of Ohio), and Isopar (registered Trade Mark) G, (a long chain saturated aliphatic hydrocarbon available from Humble Oil Company of New Jersey). Good quality images are produced with voltages ranging from 300 to 5,000 volts in the apparatus of the figure.

In a monochromatic system, particles of a single composition are dispersed in the carrier liquid and exposed to a black-and-white image. A single color results, corresponding to conventional black-and-white photography. In a polychromatic system, the particles are selected so that those of different colors respond to different wavelengths in the visible spectrum corresponding to their principal absorption bands. Also, the pigments should be selected so that their spectral response curves do not have substantial overlap, thus allowing for color separation and subtractive multicolor image formation. In a typical multicolor system, the particle dispersion should include cyan colored particles sensitive mainly to red light, magenta particles sensitive mainly to green light and yellow colored particles sensitive mainly to blue light. When mixed together in a carrier liquid, these particles produce a black appearing liquid. When one or more of the particles are caused to migrate from base electrode 1 toward an upper electrode, they leave behind particles which produce a color equivalent to the color of the impinging light. Thus, for example, red light exposure causes the cyan colored pigment to migrate, leaving behind the magenta and yellow pigments which combine to produce red in the final image. In the same manner, blue and green colors are reproduced by removal of yellow and magenta, respectively. When white light impinges upon the mix, all pigments migrate, leaving behind the color of the white or transparent substrate. No exposure leaves behind all pigments which combine to produce a black image. This is an ideal technique of subtractive color imaging in that the particles are not only each composed of a single component, but in addition, they perform the dual functions of final image colorant and photosensitive medium.

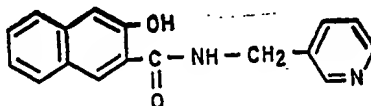
Pigments of the class of yellow and orange benzobrazanquinone pigments discussed above, are surprisingly effective when used in either a single or multicolor electrophoretic imaging system. Their good spectral response and high photosensitivity result in dense, brilliant images. It is known that, in general, cyan and magenta pigment particles separate from the trimix more easily and form more dense images than do the usual yellow pigments. The novel pigments of the present invention, however, have surprisingly good color separation and image density characteristics.

Any suitable different colored photosensitive pigment particles having the desired spectral responses may be used with the benzobrazanquinone pigments of this invention to form a particle suspension in a carrier liquid for color imaging. From 2 to 10 percent pigment by weight have been found to produce good results. The addition of small amounts (generally ranging from 0.5 to 5 mol per cent) of electron donors or acceptors to the suspensions may impart significant increases in system photosensitivity.

The following Examples further define and describe methods of making the compounds of the present invention. Parts and percentages are by weight unless otherwise indicated. The Examples below should be considered to illustrate various preferred embodiments of the invention.

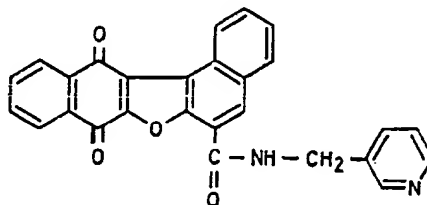
EXAMPLE I

About 30 parts of 2,3-dichloro-1,4-naphthoquinone is refluxed in 200 parts isopropyl alcohol with about 35 parts of an anilide having the formula:



About 42 parts triethylamine are added dropwise with stirring over the period of about

1 hour. Reflux is continued for about 1 hour. The solution is filtered while warm. The product is then washed with isopropyl alcohol and recrystallized from dimethyl formamide. These results about 16 parts of a yellow pigment having the formula:

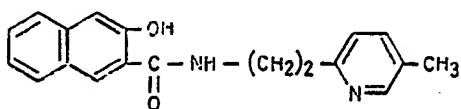


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EXAMPLE II

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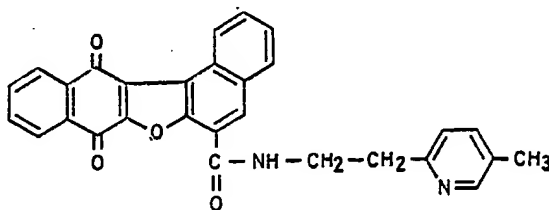
About 25 parts of 2,3-dichloro-1,4-naphthoquinone is refluxed in about 200 parts isopropyl alcohol with about 25 parts of an anilide having the formula:



10

About 35 parts of triethylamine are added dropwise with stirring over the period of about 1 hour. Reflux is continued for about 1 hour. The solution is cooled to room temperature and the product is removed by filtration. The product is washed with isopropyl alcohol. There results about 16 parts of a yellow pigment having the formula:

10

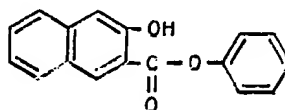


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EXAMPLE III

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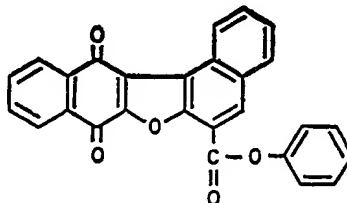
About 10 parts of 2,3-dichloro-1,4-naphthoquinone is refluxed in about 50 parts of pyridine with about 11.5 parts of an ester having the formula:



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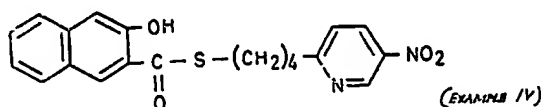
After about 1 hour the solution is cooled, the resulting precipitate is filtered and washed with isopropyl alcohol. The product is recrystallized from dimethylformamide to give about 8 parts of an orange ester pigment having the formula:

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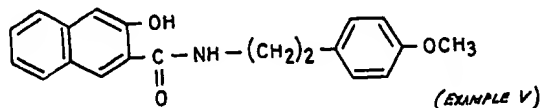


EXAMPLES IV—V

Example I is repeated two successive times using the following anilides, respectively:

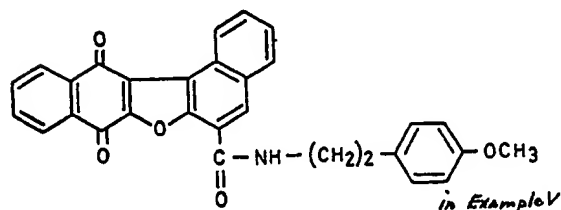
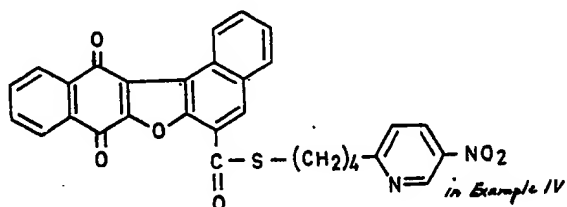


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In each case (IV—V) there results a yellow pigment, having the following respective formulas:



10 The following Examples further specifically define the present invention with respect to the use of the compounds of the general formula given above in electro-
phoretic imaging processes. Parts and percentages are by weight unless otherwise
indicated. The Examples below are intended to illustrate various preferred embodi-
ments of the electrophoretic imaging process of the present invention.

10

15 The following Examples are carried out in an apparatus of the general type illustrated in the figure with the imaging mix 4 coated on a NESA glass substrate through
which exposure is made. The NESA glass surface is connected in series with a switch,
a potential source, and the conductive center of a roller having a coating of Baryta
paper on its surface. The roller is approximately 2½ inches in diameter and is moved
20 across the plate surface at about 1.45 centimeters per second. The plate employed is
roughly 3 inches square and is exposed with a light intensity of 8,000 foot candles as
measured on the uncoated NESA glass surface. Unless otherwise indicated, 7 per cent
by weight of the indicated pigments in each example are suspended in Sohio Odorless
Solvent 3440 and the magnitude of the applied potential is 2500 volts. All pigments
25 which have a relatively large particle size as made are ground in a ball mill for 48
hours to reduce their size to provide a more stable dispersion which improves the res-
olution of the final images. The exposure is made with a 3200°K. lamp through a 0.30
neutral density step wedge filter to measure the sensitivity of the suspensions to white

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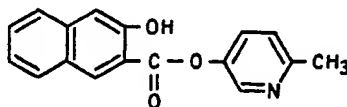
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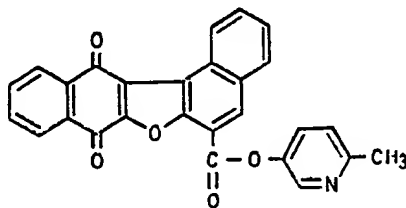
light and then Wratten filters 29, 61 and 47b are individually superimposed over the light source in separate tests to measure the sensitivity of the suspensions to red, green, and blue light, respectively.

EXAMPLE VI

Example III is repeated using an ester having the formula :



An orange pigment results having the formula :



EXAMPLE VII

About 7 parts of pigment prepared in Example I are suspended in about 100 parts Sohio Odorless Solvent 3440. The mixture is coated on a NESA glass substrate and a negative potential is imposed on the roller electrode. The plate is exposed through a Wratten 29 filter and a neutral density step wedge filter, thus exposing the plate to red light. The pigment is found to be completely insensitive to the red light. The above steps are then repeated utilizing Wratten 61, Wratten 47b and no filter to test for sensitivity to green, blue and white light, respectively. The pigment is insensitive to green light but equally sensitive to blue and white lights. When exposed to blue or white light, the suspension has good photographic speed and yields images of good density.

EXAMPLE VIII

A series of tests is run as in Example VII above, except that the pigment here is the carboxamide prepared in Example II. Again the suspension is found to be equally sensitive to blue and white light and insensitive to green and red light. The suspension has satisfactory photographic speed and image density.

EXAMPLE IX

A series of tests is run as in Example VII above, except that the pigment comprises the orange ester prepared in Example III. Again, the suspension is found to be equally sensitive to white and blue light, but insensitive to green and red light. Good photographic speed and good image density are observed.

In each of the following Examples, a suspension including equal amounts of three different colored pigments is made up by dispersing the pigments in finely divided form in Sohio Odorless Solvent 3440 so that the pigments constitute about 8% of the mixture. This mixture may be referred to as a "tri-mix". The mixtures are individually tested by coating them on a NESA glass substrate and exposing them as in Example VII above, except that a multicolor "Kodachrome" (registered Trade Mark) transparency is interposed between the light source and the plate instead of the neutral density and Wratten filters. Thus, a multicolored image is projected on the plate as the roller moves across the surface of the coated NESA glass substrate. A Baryta paper blocking electrode is employed and the roller is held at a negative potential of about 2500 volts with respect to the substrate. The roller is passed over the substrate six times, being cleaned after each pass. Potential application and exposure are both continued during the entire period of the six passes by the roller. After completion of the six passes, the quality of the image left on the substrate is evaluated as to density and color separation.

EXAMPLE X

The pigment mix consists of, as a magenta pigment, Watchung Red B, a barium salt of 1-(4'-methyl-5'-chloroazobenzene-2'-sulfonic acid)-2-hydroxy-3-naphthoic acid, C.I. No. 15865, available from DuPont; as a cyan pigment, Monolite Fast Blue GS, the alpha form of metal free phthalocyanine, C.I. No. 74100, available from the Arnold Hoffman Company; and as a yellow pigment, the carboxamide prepared in Example I. This tri-mix, when exposed to a multicolored image, produces a full color image with excellent density and color separation.

EXAMPLE XI

The pigment mixture consists of, as a magenta pigment, Locarno Red X-1686, C.I. No. 15865, 1-(4'-methyl-5'-chloroazobenzene-2'-sulfonic acid)-2-hydroxy-3-naphthoic acid, available from American Cyanamide; as a cyan pigment, Cyan Blue GTNF, the beta form of copper phthalocyanine, C.I. No. 74160, available from Collway Colors; and as a yellow pigment, the carboxamide prepared in Example I. This tri-mix is exposed to a multicolored image and produces a full color image of excellent density and color separation.

EXAMPLE XII

The pigment mixture consists of a magenta pigment, Naphtho Red B, 1-(2'-methoxy-5'-nitrophenylazo)-2-hydroxy-3''-nitro-3-naphthanilide, C.I. No. 12355, available from Collway Colors; a cyan pigment, a polychloro substituted copper phthalocyanine, C.I. No. 74260, available from Imperial Color and Chemical Company; and as a yellow pigment, the pigment prepared in Example IV. This tri-mix is exposed to a multicolored image and produces a full color image of good density and color separation.

EXAMPLE XIII

The pigment mixture consists of a magenta pigment Vulcan Fast Red BBE Toner 35-2201, 3,3'-dimethoxy-4,4'-biphenyl-bis(1''-phenyl-3''-methyl-4''-azo-2''-perylene-5''-one), C.I. No. 21200, available from Collway Colors; a cyan pigment, Cyan Blue, 3,3'-methoxy-4,4'-diphenyl-bis(1''-azo-2''-hydroxy-3''-naphthanilide), C.I. No. 21180, available from Harmon Colors; and as a yellow pigment, the pigment prepared in Example V. This tri-mix is exposed to a multicolored image and produces a full color image of good density and color separation.

EXAMPLE XIV

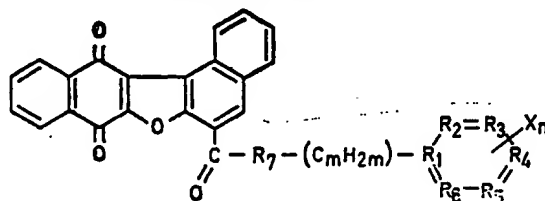
The pigment suspension consists of a magenta pigment Indofast Brilliant Scarlet Toner, 3,4,9,10-bis(N,N'-p-methoxyphenyl-imido)-perylene, C.I. No. 71140, available from Harmon Colors; a cyan pigment, Monolite Fast Blue GS, the alpha form of metal free phthalocyanine, C.I. No. 74100, available from the Arnold Hoffman Company; and as a yellow pigment, the pigment prepared in Example II. This tri-mix is exposed to a multi-colored image and produces a full color image of satisfactory density and good color separation.

As shown by the above Examples, the class of benzobrazanquinone pigments of the present invention, in general, are suitable for use in electrophoretic imaging processes. Since their photographic speed, density characteristics and color characteristics vary, a mixture of the particular pigments may be preferred for specific uses. Some characteristics of the pigments may be improved by particular purification processes, recrystallization processes and dye sensitization.

Although specific components and proportions have been described in the above Examples, other suitable materials, as listed above, may be used with similar results. In addition, other materials may be added to the pigment compositions to synergize, enhance, or otherwise modify their properties. The pigment compositions of this invention may be dye sensitized, if desired, or may be mixed with other photosensitive materials, both organic and inorganic.

WHAT WE CLAIM IS:—

1. A compound having the general formula:



wherein:

R_7 is NH , O , S or Se ;
Each of the R 's R_1 to R_6 independently is N or CH , from 0—4 of the R 's R_1 to R_6 being N ;

Each X independently is alkyl aryl, alkoxy, carboxylic acid, carboxylic ester, CF_3 , NO_2 , CN , SO_2NH_2 , $SO_2NHC_6H_5$, Cl , Br , F , I or H ;

m is a positive integer from 0—10 when $R_7=NH$ and from 1—10 when $R_7=NH$; and

n is a positive integer from 1—5.

2. The compound of Claim 1 wherein each X independently is H or CH_3 .

3. The compound of Claim 1 wherein each X is H .

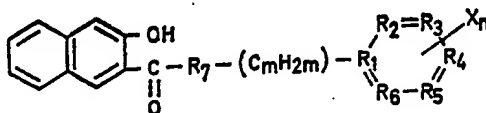
4. The compound of any one of claims 1 to 3 wherein $m=1$.

5. The compound of any one of claims 1 to 3 wherein $m=2$.

6. The compound of any one of Claims 1 to 5, wherein from 1 to 3 of the R 's R_1 to $R_6=N$.

7. A compound according to claim 1 having a formula as shown in any one of the foregoing Examples I to VI.

8. A method for the preparation of a benzobrazanquinone compound in accordance with claim 1, the method comprising reacting 2,3-dichloro-1,4-naphthoquinone with a compound having the formula:



wherein R_1 to R_6 , X , m and n are as defined in claim 1.

9. A method according to claim 8 substantially as described in any one of the foregoing Examples I to VI.

10. A process of electrophoretic imaging comprising subjecting a layer of a suspension to an applied electric field between at least two electrodes, and simultaneously exposing said suspension to an image of activating electromagnetic radiation whereby a pigment image made up of migrated particles is formed on at least one of said electrodes; said suspension comprising a plurality of finely divided particles of at least one color, the particles of one color comprising a benzobrazanquinone compound in accordance with claim 1.

11. The process of Claim 10 wherein at least one of the electrodes is at least partially transparent, and said suspension is exposed to said image through said transparent electrode.

12. The process of Claim 10 or Claim 11 wherein at least one of the electrodes is a blocking electrode.

13. The process of any one of Claims 10 to 12 wherein said suspension comprises a plurality of finely divided particles of at least two different colors in an insulating carrier liquid, the particles of each color comprising a photosensitive pigment whose principal light absorption band substantially coincides with its principal photosensitive response.

14. The process of any one of Claims 10 to 13 wherein each X independently is H or CH_3 .

15. The process of any one of Claims 10 to 13 wherein each X is H .

16. The process of any one of claims 10 to 15 wherein $m=1$.

17. The process of any one of Claims 10 to 15 wherein $m=2$.

18. The process of any one of Claims 8 to 15 wherein from 1 to 3 of the R 's R_1 to $R_6=N$.

19. A process of electrophoretic imaging, the process being substantially as described in any one of the foregoing Examples X to XIV.

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